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**Corrosion Resistant Coatings for Silicon Carbide Heat
Exchanger Tubes - Volume III**

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CORROSION RESISTANT COATINGS FOR SILICON CARBIDE HEAT EXCHANGER TUBES

1.0 SUMMARY

The development of a silicon carbide (SiC) heat exchanger is a critical step in the development of the Externally-Fired Combined Cycle (EFCC) power system. SiC is the only material that provides the necessary combination of resistance to creep, thermal shock, and oxidation. While the SiC structural materials provide the thermomechanical and thermophysical properties needed for an efficient system, the mechanical properties of the SiC tubes are severely degraded through corrosion by the coal combustion products. To obtain the necessary service life of thousands of hours at temperature, a protective coating is needed that is stable with both the SiC tube and the coal combustion products, resists erosion from the particle laden gas stream, is thermal shock resistant, adheres to SiC during repeated thermal shocks (start-up, process upsets, shut-down), and allows the EFCC system to be cost competitive. This demanding set of technical performance and cost drivers was used in reviewing and selecting candidate protective materials. After a review of open literature, discussion with leading researchers in materials for coal combustion environments, and preliminary thermodynamic studies, a total of ten materials were identified for future study that were grouped into three categories: alumina-based materials, materials stable with SiO_2 , and low expansion materials.

2.0 BACKGROUND

The EFCC Program is intended to demonstrate a direct-coal combustion combined cycle power system^{1,2}. To achieve power plant efficiencies in excess of 45 percent, high pressure air heaters capable of driving modern gas turbines from gas streams containing the products of coal combustion are necessary². It is anticipated that an air temperature of at least 1100°C will be necessary, and that the exterior tube surface may see temperatures of 1370°C. The heat exchanger will be pressurized to 100 psi, and must provide a service life of thousands of hours at these thermomechanical loads and in a coal combustion gas stream. The developers of the EFCC system have evaluated a number of ceramic materials, including monolithic oxides, discontinuously reinforced composites, and continuous-fiber ceramic composites (CFCC). The preferred materials for the tubes are reaction-bonded silicon carbide (RBSiC) and sintered SiC, because of their creep and thermal shock resistance³. Another attractive feature of SiC is its hardness at elevated temperatures. It is expected that particles approximately 30 μm in diameter will be entrained in the gas stream and impact the tubes³.

Numerous studies have shown that SiC is attacked by coal slag and that its mechanical properties are significantly degraded with time^{4,5,6,7,8,9,10}. Other ceramics, such as DuPont Lanxide's DiMOX ($\text{SiC}_p/\text{Al}_2\text{O}_3$) hold up well to the corrosive environment^{11,12}, but do not have the necessary creep resistance at the operating temperature. Selection of a protective coating is difficult because of the narrow range of thermophysical properties (coefficient of thermal expansion match with SiC, high-melting temperature, erosion resistance, high thermal shock resistance) and highly complex thermochemical application environment. At 1370°C, most coal slags are molten, and the composition of the slag changes depending upon the source of the coal.

Unfortunately, a power plant cannot run with coal from only one source. The University of North Dakota - Energy and Environmental Research Center (UND-EERC) has done extensive work on coal ash and its effect on ceramics. The factors influencing the corrosion of ceramics in coal-combustion environments was reviewed by Hurley¹³, and UND-EERC has established a stockpile of ash samples to aide in establishing a common basis for materials evaluation.

3.0 REVIEW OF CURRENT PROTECTIVE COATING EFFORTS

The identification of materials to withstand the coal slag environment has been the focus of a number of DOE programs, including Combustion 2000, EFCC, Ceramic Technology for Advanced Heat Engines and many other efforts. Research has also been done on materials for glass melting furnaces (glasses have many of the same constituents as coal slag), and a variety of other combustion applications. A brief review of the results of our literature review and discussions with researchers in this field follows.

The Ceramic Technology for Advanced Heat Engines Program is an ongoing DOE effort run through Oak Ridge National Laboratory (ORNL) that covers a broad range of ceramics issues, including protective coatings. This effort is focused toward the demonstration of ceramic components in diesel and turbine engines. The major emphasis is on Si_3N_4 ceramics. The identification of thermal and wear coatings for the Si_3N_4 components is a major effort within the program. A key difficulty with identification of materials to protect Si_3N_4 is its low coefficient of thermal expansion (CTE) of approximately 3 ppm/ $^{\circ}\text{C}$. Stinton *et al.*¹⁴ listed a series of candidate coatings which have CTEs comparable to Si_3N_4 and that may offer improved thermal resistance. These materials are shown in Table 1. The evaluation of these materials for corrosion resistance is continuing at ORNL. Results for the stability of Ta_2O_5 in sodium were presented by Lee *et al.*¹⁵ as part of this program. They showed the rapid formation of the compound NaTaO_3 at 1000 $^{\circ}\text{C}$. While NaTaO_3 is refractory, (melting temperature or $T=1810^{\circ}\text{C}$), they found that it was water soluble, and that the Ta_2O_5 - Si_3N_4 system begins to lose weight when heated above 1300 $^{\circ}\text{C}$. Fabrication and testing of test samples from the other candidate materials is ongoing.

Table 1 - Candidate Thermal and Wear Coatings for Si_3N_4 (after Stinton *et al.*¹⁴)

| Compound | Density (g/cm ³) | CTE (ppm/ $^{\circ}\text{C}$) |
|--|------------------------------|--------------------------------|
| $\text{Al}_2\text{O}_3^{\text{a}}$ | 3.97 | 8.0 |
| $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ | 2.8 | 5.7 |
| SiC^{a} | 3.21 | 5.5 |
| ZrTiO_4 | ~5 | ~4 |
| HfTiO_4 | ~5 | ~4 |
| Ta_2O_5 | 8.02 | 3.6 |
| $\text{Si}_3\text{N}_4^{\text{a}}$ | 3.19 | 3.0 |
| Al_2TiO_5 | 3.68 | 2.2 |

^aIncluded only as a reference and not as a potential coating

As part of DOE-Advanced Research & Technology Development activities, the performance of $\text{SiC}_p/\text{Al}_2\text{O}_3$ composites were evaluated in the combustion environment for a coal-fired magnetohydrodynamic (MHD) system¹⁶. In addition to the coal combustion products, MHD systems add a "seed" material to increase the efficiency of the system. In this case, potassium was used to "seed" the combustion gas stream. The $\text{SiC}_p/\text{Al}_2\text{O}_3$ composites were produced by DuPont Lanxide using the directed metal oxidation, or DiMOX, process. The tubular specimens were heated to 1230°C and were directly exposed to the coal slag, combustion gases, and potassium "seed" for 107 hours. Mechanical and microscopic examination of the tubes after exposure showed a greater variance in tube strength, but no reported interaction with the coal slag. An increase in bulk porosity was noted, but this apparently was not caused by corrosion of the DiMOX tubes.

DiMOX $\text{SiC}_p/\text{Al}_2\text{O}_3$ samples were also evaluated by Sundaram *et al.*¹⁷ for corrosion resistance in molten soda-lime glass heated to 1565°C for up to 48 hours. The glass had a composition of 73.3 weight percent (w/o) SiO_2 , 13.3 w/o Na_2O , 11 w/o CaO , 1.5 w/o Al_2O_3 , 0.3 w/o K_2O , 0.2 w/o MgO , 0.2 w/o SO_3 , 0.2 w/o ZrO_2 , and 0.07 w/o Fe_2O_3 . In their study they found that bubbles formed at the glass- $\text{SiC}_p/\text{Al}_2\text{O}_3$ interface which they attributed to the oxidation of the SiC particulates. The bubbles in contact with the $\text{SiC}_p/\text{Al}_2\text{O}_3$ were taken to be an indication of "drilling", where convection driven by surface tension gradients sweeps fresh glass to the interface and corrosion products away. The recession rates for $\text{SiC}_p/\text{Al}_2\text{O}_3$, Mo, MoSi_2 , and the candidate crucible materials they evaluated for this study are presented in Table 2. It was proposed that the SiC phase did form a silica layer upon interaction with the melt, but that it was dissolved into the glass.

Table 2 - Recession Rate in Soda-Lime-Silicate after 48 Hours at 1565°C
(after Sundaram¹⁷)

| Material | Rate (mm) at Glass line | Rate (mm) half-down |
|--------------------------------------|----------------------------|------------------------|
| AZS | 0.5 | 0.12 |
| Chromia (F) | 0.8 | 0.3 |
| Chromia (B) | 0.6 | n/r |
| MgO-PSZ | 2.8 | n/r |
| $\text{SiC}_p/\text{Al}_2\text{O}_3$ | 1.25 | 0.27 |
| Mo | n/r | 0.1 |
| MoSi_2 | 1.0 | 0.33 |

Note: n/r = not reported, F = fusion cast, B = bonded

Discussion with researchers within the DOE Combustion 2000 Program, showed that the designs of the high-temperature air furnaces (HITAF) for these systems look to avoid direct contact between the combustion gas stream and the heat exchanger tubes. These programs they are not focusing on corrosion resistant coatings for ceramic heat exchanger tubes.

van Roode *et al.*¹⁸ selected a series of oxide coatings selected for their chemical stability to 1300°C, CTE match with SiC, low modulus of elasticity, and commercial availability of powder. The selected coatings were deposited by plasma spray onto both monolithic and SiC-fiber reinforced SiC-matrix composites (SiC/SiC). Samples were corrosion tested by ORNL. The coatings used in this effort are shown in Table 3. They reported that after exposure of these materials on monolithic SiC substrates to 1200°C for between 150 and 500 hours in a 21.3 w/o O₂, 4.2 w/o H₂O, 0.04 w/o Na₂CO₃, and a balance of N₂, all of the coatings except the graded mullite-alumina system showed obvious signs of degradation.

Table 3 - Coatings Evaluated on SiC Substrates (after van Roode *et al.*¹⁷)

| Composition | Thickness (mm) | Composition | Thickness (mm) |
|-------------|----------------|-------------|----------------|
| M/VPC | 0.50 | MZ | 0.50 |
| M1 | 0.50 | MZ/A | 0.62 |
| M2 | 0.75 | MZ/A/YZ | 1.05 |
| M/A | 0.75 | M/Y | 0.75 |
| M/A/YZ | 1.05 | M/YZ | 0.88 |

M = mullite; A = alumina; Y = yttria; YZ = yttria-stabilized zirconia; Z = zircon; M/A = graded mullite/alumina coating, etc.; MZ = 50% mullite/50% zircon blend, VPC = vitreous phase ceramic seal coat.

In the same effort, mullite, mullite/alumina, and mullite/hafnia coatings were applied to SiC/SiC composites and heated for 200 hours at 1000°C in an atmosphere of 73.5 percent N₂, 22.6 percent O₂, 1.3 percent Ar, 2.6 percent H₂O, and 0.02 percent Na₂CO₃. van Roode reported that, within experimental error, the coated specimens showed no measurable recession compared to 0.53 mm recession for the SiC/SiC composite.

The development of a crystalline mullite coating by thermal spray¹⁹ is a significant development for the protection of SiC structures. Until this effort, mullite thermal spray coatings were typically amorphous, or contained a significant fraction of amorphous material. Upon heating, the amorphous coating would crystallize and undergo a volume reduction which created cracks in the coating. The effort by Lee *et al.* demonstrated greatly improved oxidation protection and thermal cyclic fatigue compared to conventional thermal spray mullite coatings.

The resistance of alumina-zirconia-silica (AZS), silica, and zircon to corrosion by the vapors of NaOH or Na₂CO₃ at 1370°C for 24 hours was determined by Bieler²⁰. He also immersed an AZS

sample in soda lime glass (74 percent SiO_2 , 3 percent Al_2O_3 , 12 percent Na_2O , 0.5 percent K_2O , and 10.5 percent CaO) at 1450°C for two weeks. After exposure to the NaOH or Na_2CO_3 vapors, the samples were visually inspected and analyzed for microstructure (scanning electron microscopy or SEM) and composition (x-ray diffraction). Substantial effects were observed on all materials with the results summarized in Table 4. As expected, the silica refractories were severely attacked by the sodium vapors. The zircon sample showed approximately 15 percent weight loss after exposure. Both AZS samples exhibited substantial bloating. For this EFCC application, bloating of a protective coating would likely cause the coating to spill, and a loss of protection for the SiC tubes.

Table 4 - Observations of Corroded Refractory Samples (after Bieler¹⁹)

| Sample | Corrosive Vapor | Volume Change (%) | Remarks (original diameter 13 mm) |
|------------------------|--------------------------|-------------------|-------------------------------------|
| Fused-Cast AZS | Na_2CO_3 | +50% | diameter swelled to 20 mm at end |
| | NaOH | +35% | uniform 18 mm diameter |
| Sinter-bonded AZS | Na_2CO_3 | +35% | diameter swelled to 19 mm at end |
| | NaOH | +25% | uniform 17 mm diameter |
| Porous sintered Zircon | Na_2CO_3 | -15% | lower end rounded |
| | NaOH | -15% | sample cracked off lid |
| Crystallized Silica | Na_2CO_3 | -65% | tapered from 7 to 13 mm in diameter |
| | NaOH | -100% | no sample remained |
| Glassy Silica | Na_2CO_3 | -70% | sample 8 to 10 mm in diameter |
| | NaOH | -95% | neck 2 mm in diameter broke off |

The corrosion resistance of an iron-magnesium-aluminum spinel ($0.25 \text{Fe}_2\text{O}_3$ - $0.75 \text{MgAl}_2\text{O}_4$) was tested by Marchant *et al.*²¹ for potential use in the MHD environment. While much of their work focused on the performance of the material as an electrode, they also exposed samples to Montana Rosebud and Illinois No. 6 coal slag that were doped with additional potassium. For the slag tests, the samples were heated to 1450°C for 24 hours and then microscopically examined using SEM and energy dispersive spectroscopy (EDS). The composition of these two slags are shown in Table 5. They found that for the Montana Rosebud slag, iron leached out of

the spinel and small amounts of silica and calcia were found in the spinel sample. The iron depletion occurred to a depth of 250 μm , and that calcium and potassium were found in the grains of the sample to this same depth. The Illinois No. 6 slag wet the sample more extensively than the Montana Rosebud material. They reported that slag appeared to penetrate along the grain boundaries. The surface of the spinel was enriched in iron and contained small amounts of silicon, calcium, and potassium. The slag along the grain boundaries was found to be enriched in magnesium and partly depleted in both iron and potassium. These effects were found by Bieler *et al.* to occur to at least 0.1 mm depth into the sample.

Table 5 - Nominal Compositions of Synthetic Coal Slags (after Marchant²⁰)

| Oxide | Montana Rosebud (mole %) | Illinois No. 6 (mole %) |
|--------------------------------|-----------------------------|----------------------------|
| SiO ₂ | 49.4 | 52.5 |
| Al ₂ O ₃ | 13.0 | 14.4 |
| CaO | 16.2 | 7.2 |
| Fe ₂ O ₃ | 3.1 | 10.6 |
| MgO | 7.1 | 3.1 |
| TiO ₂ | 0.6 | 0.9 |
| K ₂ O | 10.0 | 10.0 |
| Na ₂ O | 0.4 | 0.8 |
| P ₂ O ₅ | 0.2 | 0.5 |

Magnesium chromite (MgCr_2O_4) has been studied as a refractory for slagging gasifiers. Wiederhorn *et al.*²² evaluated the stability of MgCr_2O_4 to synthetic western, anorthite, and diopside slags at 1500°C for 24 hours, and compared these results to a MgCr_2O_4 brick obtained from a gasifier plant which operated on a variety of coals. The composition of the synthetic slags used in their study are shown in Table 6. During their study, they identified/confirmed a number of interactions between the MgCr_2O_4 and coal slag. Their results can be summarized as:

- Iron and aluminum enter into the MgCr_2O_4 grains via solid-state diffusion
- Cr_2O_3 is slightly soluble (~3 percent) in the slag
- MgO is leached from the refractory by the slag during high temperature exposure, and is drawn away through the vitreous intergranular phase
- Exposure of the MgCr_2O_4 to the synthetic coal slag resulted in the formation of a dense spinel containing MgO, Cr_2O_3 , Al_2O_3 , and FeO
- In the anorthite slag, the exposed surface of the refractory was completely depleted of MgO and a corundum structure (6 w/o Al_2O_3 and 94 w/o Cr_2O_3) was formed
- The diopside slag completely reacted the MgCr_2O_4 in 24 hours at 1500°C

Table 6 - Composition of Slags Used in Laboratory Studies

(after Wiederhorn *et al.*²¹)

| Slag | CaO | Al ₂ O ₃ | SiO ₂ | FeO | MgO | Na ₂ O |
|-----------|-----|--------------------------------|------------------|-----|-----|-------------------|
| Synthetic | 16 | 17 | 53 | 6 | 4 | 3 |
| Anorthite | 22 | 22 | 56 | 0 | 0 | 0 |
| Diopside | 26 | 0 | 55 | 0 | 16 | 0 |

Note: All compositions are listed in weight percent

The addition of chromia to alumina-silica refractories has been known to increase slag resistance, with Chan and Ko²³ performing a recent study. They found that the addition of Cr₂O₃ enhance the slag resistance by increasing the viscosity of the slag, and, therefore, reducing its reactivity and its ability to penetrate the refractory. An additional effect of the increase in slag viscosity is a reduce mullite formation rate. Chan and Ko site that the rate of mullite formation is dictated by the transport of silica through the liquid phase, so increasing the viscosity of the slag retards this reaction. It must be noted that the slag used in their study contained very high levels of CaO (59.4 w/o) and was to be representative of a torpedo ladle environment.

The thermal stability of a variety of ceramics in the natural gas combustion environment was performed by Lin *et al.*²⁴ by heating samples to 1370°C and 1600°C for 50 hours and 56 hours, respectively. The materials they evaluated included AZS, fusion-cast and bonded chromia, Al₂TiO₅-mullite composite, and SiC_p/Al₂O₃. The performance criteria for these materials in their study was the weight-loss over time. The results of their study are summarized in Table 7. In the environment used by Lin *et al.*, the aluminosilicate glassy phase present on the surface of the SiC_p/Al₂O₃ was believed to be fluid enough to allow the formation of CO bubbles. They proposed that these bubbles created periodic interruptions in the glassy layer which led to the unending weight gain. The continuous weight gain for the AZS at 1600°C was attributed to extrusion of the glassy phase in the material. The force for the extrusion is thought to come from gas bubble formation within the AZS and the volume change associated with the zirconia transformation. Lin *et al.* observed debris on the surface of the sample which they attributed to this process. The Al₂TiO₅-mullite composite examined in the study showed excellent behavior at both temperatures, and the weight loss exhibited by the samples was attributed to the oxidation of the small amount of residual carbon in the samples. For both chromia-based materials, the continuous weight loss was attributed to the oxidation of Cr₂O₃ to CrO_{2(g)}. The difference in rates between the bonded and fusion-cast materials was attributed by the authors to the presence of a spinel-phase in the fusion-cast material, which offered some protection to the Cr₂O₃. Since the weight loss at 1370°C was severe, the investigators did not test the chromia samples at 1600°C.

Table 7- Results of High-Temperature Exposure Tests (after Lin *et al.*²⁴)

| Material | 1370°C Weight * Change (mg/cm²) | 1600°C Weight ** Change (mg/cm²) |
|--|---|--|
| AZS | 0.39 | 0.149mg/cm ² -h # |
| Chromia (F) | 0.046mg/cm ² -h # | n/r |
| Chromia (B) | 0.154mg/cm ² -h # | n/r |
| Al₂TiO₅-mullite | 0.43 | 0.6 |
| SiC_p/Al₂O₃ | 0.012mg/cm ² -h # | 0.083mg/cm ² -h # |

- denotes linear oxidation rate; n/r = not reported

* - weight change in 50 hours; ** - weight change in 56 hours

4.0 TECHNICAL APPROACH

As stated previously, the goal of this effort is to identify up to 10 materials that may provide the balance of performance and affordability (raw materials and processing) needed for the EFCC application. Future work would experimentally evaluate the corrosion and erosion resistance of the candidate materials identified in this effort.

For initial demonstration in the EFCC system, the goal for a protective coating approximately 0.1 inches thick would be to protect the SiC tubes for 1,000 hours of operation. Obviously, to become commercially viable the life of the coating must be substantially longer than 1,000 hours. To obtain the necessary service life of thousands of hours at temperature, a protective coating is needed that is stable with both the SiC tube and the coal combustion products, resists erosion from the particle laden gas stream, is thermal shock resistant, adheres to SiC during repeated thermal shocks (start-up, process upsets, shut-down), and allows the EFCC system to be cost competitive. Thus, identifying a material/deposition set for processing these thick coatings is required.

4.1 Materials Selection Process

The approach used in our materials selection was to review current literature and research efforts related to this problem, as discussed in Section 3.0, and complement this effort with thermodynamic modeling and review of existing phase diagram information. After discussion with Stinton of ORNL, Natesan of ANL, and others, we identified three classes of protective coatings: 1) alumina-based materials, 2) materials stable with silica, and 3) materials with a low CTE. Our goal was then to identify candidate materials that fit into each of these classes that also may be expected to provide the required balance of thermophysical properties, thermochemical stability, and lower processing costs.

The first element in selecting materials for this application is understanding the environment the coatings will see. The environment for the EFCC heat exchanger is high-temperature (up to 1370°C), and oxidizing. Molten coal slag particles impinge on one side of the tubes (predominantly) and flow down the tube. The entire tube length is exposed to hot combustion gases, and unmelted particles impinged along the entire tube length. The coal slag composition varies with the source of the coal. For this effort, a slag composition was identified by Hurley²⁵ for which a sample was available for later testing, and that would be typical of the high combustion temperature projected for the EFCC system. The composition of this ash is provided in Table 8. The slag from the Baldwin Plant is from an Illinois No. 6 coal that had been fired in a cyclone combustor at a temperature of over 1300°C. With this high firing temperature, no sodium is present in the slag. This was a key consideration in the selection of materials.

Table 8 - Chemical Composition of Baldwin Slag (after Hurley²⁵)

| Oxide (weight percent) | Baldwin Slag |
|--------------------------------|-----------------|
| SiO ₂ | 53.4 |
| Al ₂ O ₃ | 18.6 |
| Fe ₂ O ₃ | 17.6 |
| TiO ₂ | 0.7 |
| P ₂ O ₅ | 0.0 |
| CaO | 7.1 |
| MgO | 0.9 |
| Na ₂ O | 0.0 |
| K ₂ O | 1.7 |
| SO ₃ | 0.0 |

A list of candidate materials was compiled based upon our literature review, discussions with other researchers, and understanding of the application environment. The literature review was used to identify promising materials from other studies and also to steer us away from system that had not worked. A basic assumption in our review of candidates was that some materials properties can be engineered to one degree or another, while others are inherent. For example, it is now accepted that the CTE and the compliance of a coating can be engineering by applying microstructural design concepts, including functionally-gradient materials, designed porosity, and composite coatings. Erosion resistance may also be modified by microstructural design and composite coatings, as demonstrated in electron-beam evaporated thermal barrier coatings. However, thermochemical stability is an inherent property of the coating material(s). So, in our review of materials, the potential for thermochemical stability was given the highest weight with the assumption that the CTE, compliance, and erosion resistance could be addressed through coating design.

All of the candidate materials were reviewed for their strengths in the following categories: 1) Chemical compatible with SiC; 2) Stability in an oxidizing environment with the slag; and 3) Potential for erosion resistance. The requirement for stability with SiC ruled out silicide formers, such as the noble and refractory metals. Stability with the ash and the oxidizing environment ruled most non-oxide ceramics, except those that form potentially stable oxide coatings. Coatings with lower oxygen transport were also desired because that will slow the growth of the silica layer on the SiC tubes. Erosion resistance is related to toughness and stiffness of the material at temperature. Unfortunately, there is very little information on these properties for most materials. However, materials with higher melting temperature and more complex crystal structure will generally exhibit greater hardness at temperature. Hillig²⁶ presents the basis for this behavior. While melting temperature and crystal structure were considered in materials selection, the lack of information on high-temperature properties of ceramics decreased the significance of erosion resistance in selecting materials.

4.2 Candidate Materials

The materials selection process led to the identification of ten candidate materials for use in future corrosion experiments. The candidate materials are summarized in Table 9 by their classification. Some features of each material are provided in the following sections.

Table 9 - Candidate Protective Materials

| Alumina-Based | Silica Stable | Low Expansion Materials | Other |
|--|----------------------------------|----------------------------------|--------------------|
| 3Al ₂ O ₃ •2SiO ₂ | BaZrO ₃ | NZP (CS-50) | CaTiO ₃ |
| Al ₂ TiO ₅ /Al ₂ O ₃ | MgCr ₂ O ₄ | ZrTiO ₄ | |
| SiC _p /Al ₂ O ₃ | YCrO ₃ | Al ₂ TiO ₅ | |

Notes: NZP = sodium zirconium phosphate - type material; CS-50 = calcium strontium variation of NZP supplied by LoTec

3Al₂O₃•2SiO₂: Mullite has been identified by ORNL, NASA, DOE-AR&TD, and many other researchers as being highly corrosion resistant, and it is expected to be resistant to coal slag. It has a very good CTE match with SiC and a lower modulus. The complex crystal structure of mullite also makes it resistant to creep.

Al₂TiO₅/Al₂O₃: Alumina is very resistant to most coal slags, but its CTE is too high (~9 ppm/°C) compared to that of SiC. The addition of aluminum titanate (CTE ~2ppm/°C) will reduce the CTE mismatch. Al₂TiO₅ is stable with silica to 1480°C (Phase Diagram for Ceramists or PDC 771), with alumina (PDC 4376), and mullite (PDC 768 and 771). Therefore, both constituents of the coating should exhibit good stability with the slag. The proportion of Al₂TiO₅ to Al₂O₃ to obtain a reasonable CTE match with SiC would need to be determined..

SiC_p/Al₂O₃: The DiMOX material has shown good resistance to slag in MHD studies. It was also evaluated by Hague for heat exchanger tubes, but it does not have the requisite creep resistance at temperature necessary for that application. The DiMOX process is not amenable to forming a coating on a SiC tube, but an analog, that should allow the deposition of this material as a coating is discussed in Section 4.3.

BaZrO₃: Barium zirconate is very refractory ($T_m=2600^{\circ}\text{C}$), has the lowest CTE (6.5 ppm/ $^{\circ}\text{C}$) of the alkaline-earth zirconates, and the barium cation should be the least mobile to slow interactions with the slag. Examination of the phase diagrams for both the BaO-ZrO₂-SiO₂ and BaO-ZrO₂-Al₂O₃ systems (PDC 4546 and 5367, respectively) shows the potential for interaction in this system. The BaO-ZrO₂-SiO₂ diagram shows that BaZrO₃ is in equilibrium with the compound 2BaO•2ZrO₂•3SiO₂ which has a melting temperature of 1380 $^{\circ}\text{C}$. For the BaO-ZrO₂-Al₂O₃ diagram, BaZrO₃ is in equilibrium with the compounds BaAl₂O₄ and Ba₃Al₂O₆. No melting temperature was included for the barium aluminate compounds. The possibility that these reactions occur was recognized in selecting the zirconate for examination. The material was included for its generally excellent chemical stability and as an alternate to chrome-based systems.

MgCr₂O₄: This material is used commercially as a refractory in slagging environments. Chromia-based materials should provide good corrosion resistance to the slag, though some leaching of the constituents is likely to occur. It has not been shown to form silicates, which is likely a critical factor in performance. It is likely that iron, aluminum, and calcium will diffuse into this material, but these compounds are all refractory. Information on the stability of spinels based on MgCrO₄ with silicates (PDC 2259 - 2265) shows a minimum eutectic temperature of over 1500 $^{\circ}\text{C}$. If the spinel becomes dominated by Fe₂O₃ (MgFe_{1.8}Cr_{0.2}O₄), the eutectic may be lowered to 1390 $^{\circ}\text{C}$. PDC 924-926 and 4640 show that MgCr₂O₄ is stable with silica, magnesium silicates, monticellite, merwinite, akermanite, and diopside, however, the temperature of the equilibrium diagrams was not indicated. The only experimental data given in the Phase Diagrams for Ceramists by the researcher was that the samples were heated to " $\sim 100^{\circ}\text{C}$ below the formation of a melt". The lack of silicate formation for the chromia-based spinels is encouraging.

YCrO₃: Yttrium chromite is a very refractory ($T_m=2290^{\circ}\text{C}$) chrome-based compound. The chrome-based systems are attractive because of the resistance of chromia to silicate formation. If YCrO₃ reacts with the slag, it would likely that yttria would form other very stable compounds with the alumina in the slag (yttrium aluminum garnet), and viscous glasses with silica (minimum melting temperature 1660 $^{\circ}\text{C}$ from PDC 2388). No phase diagrams were available for yttria interaction with K₂O.

NZP (CS-50): The experimental works of Natesan and Stinton have yielded encouraging results for this material at somewhat lower temperatures in coal combustion environments. The thermal expansion and mechanical properties of this class of material was studied extensively by Hirschfeld and Brown²⁷. The CS-50 composition supplied by LoTec has performed well in other experiments, has a low CTE, and a low modulus. Based upon the recommendation of Natesan and Stinton, this materials has been included in this study.

ZrTiO₄: Zirconium titanate was identified by ORNL in their search for protective coatings for Si₃N₄. ZrTiO₄ is refractory with a melting temperature of approximately 1900°C. Titania does not react with silica, though some solubility is expected. Other potential reaction products of this material with the coal slag are generally refractory also, including zircon, aluminum titanate, calcium titanate, calcium zirconate, etc. The reported linear thermal expansion of Zr_{0.6}Ti_{0.4}O₄ has been reported as 0.2 percent at 1200°C. The combination of expected thermochemical stability and low CTE make this system attractive.

Al₂TiO₅: Aluminum titanate was identified by ORNL in their search for protective coatings for Si₃N₄. As discussed in the Al₂TiO₅/Al₂O₃ section, Al₂TiO₅ is expected to be resistant to many of the slag components. Its low CTE and very low modulus, which results from a highly microcracked structure, are also attractive features. An alternative to this material would be the mullite/Al₂TiO₅ composite described by Lin *et al.*²⁴ and Hirschfeld and Brown²⁶.

CaTiO₃: Calcium titanate is used in gas turbines to provide corrosion protection on selected components. CaTiO₃ is refractory (T_m = 1970°C) and offers good stability with many of the slag components, including variety of calcium and calcium magnesium silicates. A concern with this system is the high potential for formation of sphene (CaTiSiO₅) when the titanate is in contact with silica at 1370°C. Sphene melts at approximately 1373°C. This is obviously too low a melting temperature to be of any use in this application. However, because of its successful use in other, lower temperature, combustion systems, this material should be considered for testing.

A material that was considered for recommendation in this study was the SiC-AlN solid solution. This system has been studied extensively by Virkar, with a representative discussion of the properties of this system given by Rafaniello *et al.*²⁸. More recently, Mroz and coworkers at Advanced Refractory Technologies (ART) have evaluated the oxidation and corrosion resistance of SiC_p/AlN composite, with the goal of forming a mullite scale. Both the solid solution and particulate composite approach offer potential longer term solutions to this corrosion of the SiC heat exchangers. Since the SiC_p/AlN system is being evaluated by ART, it was not selected for this effort.

4.3 Coating Deposition Processes

The EFCC system uses a heat exchanger with a total span of approximately 16 feet. Thus, the heat exchanger tubes are expected to be between 6 feet long and 16 feet long with a diameter of approximately 3 inches. Obviously, if 6-foot-long tubes are used they will be joined in some fashion. In either case, the protective coating must be applied to a large structure with a production volume goal of thousands of feet per year. We reviewed the benefits and limitations of a broad range of coating processes, including chemical vapor deposition (CVD), physical vapor deposition (PVD), thermal spray, sol-gel, slurry processing, electrophoretic, and laser cladding, for depositing protective coatings onto these tubes and brief comments on each process are provided.

CVD has been used to coat and fabricate long tubes using a variety of materials. With sufficient development, 6-foot-long tubes can be coated uniformly and a moderately efficient use of

precursors can be achieved by using a cold-wall deposition system (i.e. the substrate is directly heated and deposition occurs only on the substrate). However, deposition of complex oxides by CVD is relatively slow, and some elements have precursors with either limited volatility or high cost. If 16-foot-long tubes are desired, a new production facility would be required, and CVD is moderately capital intensive. CVD can deposit thick (0.1 inch) films within moderate processing times (hours). Coating uniformity (thickness and composition) are issues that would require significant development. CVD does allow processing at high temperature, which provides for a strong bond to the substrate. In general, CVD could be used for this application, but it is not a leading candidate because other processes to deposit oxides are lower cost and existing equipment is available for processing even 16-foot-long tubes.

PVD (sputtering and evaporation) are not generally used to deposit thick coatings. The advent of electron beam PVD (EBPVD) for deposition of thermal barrier coatings is an exception to this rule. PVD offers excellent control of film composition and morphology, but deposition rates are often low. EBPVD does achieve high deposition rates for oxides. PVD system require high-vacuum chambers (10^{-6} to 10^{-8} torr base pressures) and are very capital intensive. PVD is not a candidate for economical deposition of thick coatings onto long tubes.

Laser cladding forms a coating by flowing powder to the intersection of a laser beam and the substrate. By controlling the powder feed rate and the power density of the beam, a coating is formed by fusing the powder to the surface of the substrate. Laser clad coatings feature a metallurgical bond between the coating and substrate. Some of the limitations of laser cladding are that the coatings are generally microcracked, due to the volume contraction upon solidification, and that multiple passes are needed to produce thick coatings. With the high degree of microcracking in these coatings, laser cladding is not a leading candidate for applying the protective coatings.

Sol-gel, slurry, and electrophoretic processes all require a sintering step to produce dense coatings. As deposited coatings will typically be between 40 and 60 percent dense, with the density being limited by the theoretical packing efficiency of the particles, the addition of binders to the system to increase green strength, and absorbed water or solvent from the process. Sintering these coatings to a high density produces substantial stresses due to coating shrinkage, which make the deposition of thick coatings difficult. All three processes are inexpensive, but multiple processing cycles may be required to produce a thick coating. These processes are viable candidates for deposition of the coatings, but may not be the preferred method.

Reaction bonding has been used to produce SiC and Si_3N_4 structures for many years. A key advantage of reaction bonding is that, by proper selection of the reactants and filler materials, very little volume change occurs during reaction. The near-net-shape capability of reaction bonding is very attractive for the formation of coatings also. Recently, a reaction bonding process for aluminum oxide (RBAO) has been studied by Claussen *et al.*²⁹ and Wu *et al.*³⁰. In this process, aluminum, aluminum oxide, SiC_p , and/or ZrO_2 are blended, pressed into a preform, and fired in air. By proper selection of the precursor ratios and firing schedule, alumina, alumina/mullite, or mullite based materials can be produced with very low (<4 percent) volume contractions. The structure of the RBAO can resemble DiMOX materials. Thus, it may be

possible to form "DiMOX" coatings using the RBAO technique. Lehigh University is also studying processing routes to other metal oxide systems. This process would be amenable to thick coatings, and seems to entail relatively simple processing equipment. While significant development would be necessary to produce RBAO-based coatings, the potential for low processing and equipment costs makes this method an attractive candidate for deposition of the coatings.

Thermal spray, which includes a variety of techniques, is routinely used to deposit thick oxide coatings onto large structures. A feedstock of the desired material is fed into the heat source, melted/softened, and accelerated towards the substrate. As it impacts the substrate, the feedstock powder splat cools. The process equipment is relatively simple and it is cost effective. The limitations of thermal spray for this application include that the coating adheres to the substrate only by mechanical interlocking of the individual "splats" with the surface, and that thermal spray of oxide coatings generally have greater than 10 percent open porosity. To improve adhesion in these coatings, a surface roughening of the substrate is necessary. A recent development at our lab, Small Particle Plasma Spray or SPPS, addresses these concerns. SPPS allows the spraying of submicron powders. Using SPPS, the coating can be made >99 percent dense and have no open porosity. The ability to deposit dense and crack free coatings is highly desirable for this application. Also, the mechanical interlocking of the coating to the substrate requires the powder particles and the surface roughness of the substrate to be the same order of magnitude. By using submicron powders, little, if any, surface preparation is needed to achieve an adherent coating. Thermal spray is routinely used to coat large rollers for the metals and printing industries that are longer than those proposed for this heat exchanger. Portable systems are also available for some of the thermal spray methods. Thermal spray, and SPPS in particular, is an attractive method for depositing the oxide coatings.

5.0 Conclusions and Recommendations

5.1 Conclusions

The following conclusions can be drawn from this study:

- Current efforts to identify corrosion-resistant materials and coatings for coal-fired power systems has focused on a relatively small group of materials.
- The performance of materials is highly dependent upon the test conditions.
- A common source of coal slag with known composition and history has not been available until the effort by UND-EERC to provide this resource.
- A systematic evaluation of the corrosion resistance of materials in a baseline environment for coal-based power systems has not been done.
- The complex composition of coal slag, the lack of thermodynamic information on many ternary and higher oxide systems, and the lack of experimental data make selection of candidate protective materials difficult.
- Thermal spray, reaction bonding, and powder/sintering-based coating methods are viable candidates for coating long tubes.

5.2 Recommendations

The following recommendations are made as a result of this study:

- An initial screening study using the 10 candidate materials selected in this effort should be performed.
- The coal slag sample for this study should come from UND-EERC so that other researchers can access the same material for comparative studies.
- The screening effort should be done on bulk samples of candidate materials, so that the expensive coating development effort is done only on the most promising systems.
- Additional materials identification, modeling, and screening efforts are needed that are focused on coal-fired power systems.
- The most promising systems from the screening evaluation should be applied to sub-scale SiC tubes for more rigorous testing, including thermal cycling, high-temperature corrosion/erosion exposure and strength retention.

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